



**High Temperature Superconductor
Materials and Applications
(5-32425)**

**Final Technical Report for the Period
July 12, 1990 through January 11, 1991**

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**High Temperature Superconductor
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Final Technical Report for the Period
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PREFACE

This technical report was prepared by the staff of the Research Institute, The University of Alabama in Huntsville. This report is to serve as documentation of technical work performed under contract number NAS8-36955, Delivery Order 89. Dr. George B. Doane was Principal Investigator. Technical work was produced by Dr. John Golben and Mr. Curtis Banks. Dr. Eugene W. Urban, Chief of the Infrared & Cryogenic Physics Branch, Astrophysics Division, Space Sciences Laboratory, Science and Engineering, MSFC/NASA, provided technical coordination.


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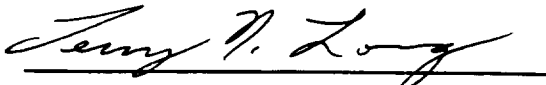
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INTRODUCTION AND OVERVIEW

The research performed during the course of this delivery order fell into two areas.

One of the areas concerned itself with the investigation of the phenomena involved in formulating and making in the laboratory new and better superconductor material with enhanced values of critical current and temperature. Of special interest were the chemistry, physical processes and environment required to attain these enhanced desirable characteristics.

The other area concerned itself with producing high temperature superconducting thin films by pulsed laser deposition techniques. Such films are potentially very useful in the detection of very low power signals. To perform this research high vacuum is required. In the course of this effort older vacuum chambers were maintained and used and in addition a new facility is being brought on line. This latter activity has been replete with the usual problems of bringing a new facility into service. Some of the problems are covered in the main body of this report.

Superconductor Material Investigations

Under this contract, efforts to enhance melt-sintering effects on high temperature superconductors were continued. This continuation primarily emphasized work on the Bi-based superconductor system which contains several high temperature superconductor phases. A vibrating sample magnetometer was also constructed, calibrated and used for the first time as a characterization method for an archive of samples.

The Bi-Based Superconductor

The Bi-based superconductor system consists of three high temperature superconductor phases. The crystal structures of these three phases are very similar. Figure 1 shows the structures for the $T_c = 22K$, $85K$, and $110K$ phases respectively. The structural addition of a Ca atom layer and a CuO_2 layer to the $22K$ phase comprises the $85K$ structure. Likewise the addition of another Ca layer and CuO_2 layer to this latter structure comprises the $110K$ structure. The chemical formula for these phases can be written $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$, $n=1,2,3$ corresponding to the $22K$, $85K$ and $110K$ phases respectively. Again, it is clear that the insertion of extra Ca and CuO_2 layers alter the structure and superconducting properties of the Bi superconductor system.

It is not surprising then, that careful control of the processing conditions for these samples permits control of which phases are present in the sample. Most often, because of the similarity in structures of these phases, all three phases are present to some degree in the average sample. In the work previously reported on, we found that the conditions involving time, nominal composition, and temperature and oxygen partial pressure (Figure 2), all contributed to the isolation of the much desired "2223" ($110K$) phase. Other factors such as heating and quenching rates and general pre-sintering conditions also were important, but these factors were not well-defined.

Much has been written about the preparation techniques for these compounds. The preparation condition for which there is still widespread confusion is that of time. Many papers claimed that extensive time was required to form the higher n -ordered phases. This time required ranged from days to weeks to months. Evidently, the degree to which other preparation factors (such as those listed above) were used were different in each group's samples. For example, it is well known that the sintering regime will be dominated by diffusion processes. These processes are characterized by exponentials involving time and temperature. Hence, maximizing the temperature that can be used for sintering, greatly reduces the time needed for the process. This is demonstrated clearly in the oxygen dependence graph (Figure 2) which shows that at the upper end of each sintering range, the 2223 phase is best formed.

For the Bi "2212" ($85K$) and "2223" ($110K$) phases, it has also been shown that the partial substitution of Pb for Bi in the compounds greatly reduces the time required to form the phases.

In most cases, the time required to form the Pb-substituted 110K phase is about 3 days. To date, the additional substitution of Sb for Bi has not reduced the needed time, but has improved the superconducting properties of the sample in some cases. Therefore, we experimented with Pb and Sb substitution in the hope that we could enhance the superconducting properties.

It is also clear, however, that the morphology of the sample before the final sintering has a lot to do with the final result. For these new Pb and Sb substituted samples, we employed some new steps in the initial preparation designed to increase sample homogeneity, and decrease particle size. After the initial powders were weighed, mixed and coarsely ground, the powders were deposited into a ball mill with ethyl alcohol and ground for several hours. This alcohol was then evaporated from the mixture by placing the sample in a furnace set at 200C. The remaining sediment was heated in powder form to 810C for 20 hours, reground in a manner similar to the original procedure, and pressed into pellets under 6000psi. X-ray diffraction scans demonstrated these preheated powders to be a mixture of 2201, 2212, and Pb/Sb-dominated phases. It is believed that the samples were homogeneous and finely dispersed.

Melt-Sintering Results

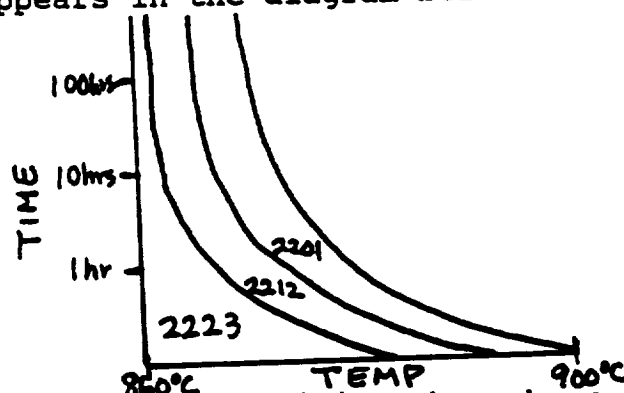
Figure 3 demonstrates that extreme orientation characteristic of the melt sintering technique can be achieved for all three phases of the Bi system. Figure (a) is an x-ray diffractogram of the 2223 phase, while (b) and (c) are scans of the 2212 and 2201 phases respectively. Note particularly the 002 indexed line near $2\theta = 5^\circ$ in all of these scans. Since increasing d-spacing is depicted in these scans as a shift toward the left, we can see that the 002 line shifts left as the structure changes from 2201 to 2212 and finally to 2223. The d-spacing is related to the unit cell size. Hence this shift in d-spacing is due to the increase in the unit cell c-parameter as the extra Ca and CuO₂ layers are added to the structure. The other dominant lines in these scans are not indexed the same, so the same shift is not expected (See Figure 4 for indexing of the 2212 and 2223 phases).

The specific melt-sintering effect for one phase is ruled by diffusion-like conditions. As an example, one particular sample which was Sb-substituted formed an oriented 2212 phase under the following conditions of time and temperature:

<u>Temp</u>	<u>Time</u>
868C	3 hrs
873C	40 min
883C	3 min
893C	2 min

Exact values of the time could not be obtained since these samples were placed in and removed from the oven very quickly. The time required for the sample to reach an equilibrium in temperature with the furnace was approximately 2 minutes.

There seems to be a reverse phase formation effect under melt-sintering conditions. For example, as a function of temperature under bulk synthesis conditions, the 2201 phase will be formed first, followed by the 2212 phase and then the 2223 phase. As a function of time the same priority will occur, though some values of time are too long to measure. Under melt-sintering conditions just above the melting temperature of the compound, the 2223 oriented phase will be formed first followed by the 2212 phase and then the 2201 phase. The melt-sintering time of the 2223 phase can be extremely minute, while longer times are possible with the other two phases. These times and temperatures involved in the melt-sintering process are again consistent with a diffusion-like relationship. Much more data on many more compositions would be required to form a quantitative analysis. However, a depiction of this idea based on some of the present data, appears in the diagram below:



After melt-sintering conditions have been applied, the usual sintering relationship can again be used to obtain a desired phase as the X-ray scans in Figure 5 demonstrate. In (a) the sample has been melt-sintered to form a very oriented 2212 film on the surface. The sample is then heated at successively increasing temperatures (but below the melting temperature) to grow the 2223 phase. Figures (b), (c), and (d) show the emergence of this latter phase as the temperature is increased to 861C, 866C, and 869C respectively. This 2223 phase can be distinguished by characteristic lines at $2\theta = 24^\circ$ and 34° .

Sb For Bi Substitution In The 2223 Phase

One particular objective of this work was to form the 2223 phase with Sb substitution for Bi in bulk form. There had been several reports of very high transition temperatures (ranging from about 130K to 160K) in samples that contained Sb in the nominal stoichiometry, but these reports could not determine which phase was actually responsible for these high transition and whether Sb was actually substituting into these phases. Th

reports of higher transition temperatures themselves were not reproduced by generally accepted reputable labs. Since X-ray diffraction data was not shown, there was no presented proof that a single phase Sb-substituted compound was formed.

Our first efforts to form this compound, using methods that were successful with the Pb-substituted compound, failed. Though some of these samples were actually high temperature superconductors, X-ray diffraction scans demonstrated these samples to consist of several phases. These extra phases primarily consisted of unreacted initial constituents, including Sb_2O_3 . These superconductors often showed very high onset transition temperatures (between 110K and 120K) but rarely obtained a zero resistance state above liquid nitrogen temperature. If these results were to be consistent with the published reports, then it would seem that the very high transition temperatures claimed might actually be due to the presence of a small amount of new phase. In our samples this would explain the presence of high onset transitions, though not enough of the superconducting phase was present to form a conductive path through a macroscopic piece of sample. However, an onset transition between 110K and 120K could also be due to a non-Sb-substituted phase and this result would be consistent with the range generally reported for the 2223 phase.

The conditions required to simply produce a high temperature superconductor with Sb present, were more strict than normally required for Bi superconductors. It was also found that, depending upon the preheated conditions, it was sometimes impossible to form a high temperature superconductor at all. The solution to the problem of forming a Sb-substituted 2223 phase rested mainly with the preheat treatment.

As mentioned previously, the sintering temperature required for the Bi system increased as the nth order of CO_2 planes in the structure increased. Contrary to some early reports, it was very beneficial to form the 2212 phase from the 2201 phase, and likewise the 2223 phase from the 2212 phase. This could be done if the proper nominal constituents were still available in the sample. Therefore, it was logical to try to form a Sb-substituted 2212 phase first and then form the 2223 phase. To synthesize the former phase, a very long heating ramp was necessary. This treatment evidently promoted homogeneous diffusion throughout the sample. A similar treatment had proven successful in attempts to substitute Sr for Ba in the 1:2:3 superconductor system.

It was also discovered that this slow ramp in temperature also helps to remove the CO_2 from the CaCO_3 constituent. A study on the thermogravimetric analysis apparatus (Figure 6) shows that at higher ramping rates, the CO_2 is released at correspondingly higher temperatures. Hence at initial heating rates of 5 C/min or higher it is very likely that a significant amount of carbonate is still present in the sample when the Bi-system phases are being formed. Since carbon has been shown to hinder superconducting properties, it is essential that an initial slow

ramp is used.

To the limits of X-ray diffraction techniques, a pure Sb-substituted 2223 phase was finally synthesized. The structure was very similar to that of the Pb-substituted phase. The properties of this phase were also very similar. No transition onset was found above 115K. This transition limit was determined from transport measurements and not magnetic measurements. In transport measurements a superconducting path must percolate through a macroscopic portion of sample in order for a transition to be observed. If one assumes that the sample is predominantly single phase, then a failure to observe a higher transition (if it existed) would mainly lie with mechanical defects and imperfections in the sample. Magnetic measurements, such as those that can be obtained from a vibrating sample magnetometer, require no actual physical contact with the sample. A signal can be obtained from a small superconducting fraction and no percolating path is necessary. Therefore it was desired to obtain these measurements.

The Vibrating Sample Magnetometer

The vibrating sample magnetometer uses a transducer to oscillate the sample at a known frequency and amplitude. As is well known, a moving magnetic sample will induce a current in stationary pickup coils. This signal will be proportional to the transducer frequency, amplitude and the magnitude of the superconductor's diamagnetism. With this technique, measurements of the superconductor's transition temperature, volume fraction and magnetic flux retention can be obtained. Only a very small amount of sample is needed and no physical contact with the sample is required. In addition to the above Sb-substituted samples, we have an archive of samples that could be investigated with this system. Hence, a significant portion of time under this contract was devoted to setting up this apparatus.

The available computer hardware and software had to be adapted to the system. Many problems were encountered and solved in this process. Likewise many external hardware connections have been made to the system. The system has been aligned, calibrated and tested. A cryogenic dewar necessary to cool samples to the superconducting state has been installed. This dewar requires helium as the coolant under normal operation, and this helium must be externally ordered. Under some conditions nitrogen can be used, but the control necessary to obtain information on the Sb samples discussed above is not possible with this coolant in this dewar setup.

Examples of the first measurements taken on superconducting samples with this apparatus appear in Figures 7 and 8. Figure 7 shows a hysteresis curve taken at 77K on a partially melt-sintered 1:2:3 sample (B365). The curve looks very similar to curves reported by other groups on sintered samples except that the area enclosed by the curve is larger as the sample becomes more melt-sintered. This is a result of more flux trapping

the melt-sintered sample as opposed to the sintered sample.

The sample zone of the dewar is superinsulated such that the heating control cannot be used if helium is not the coolant (otherwise permanent electrical damage would result). Using liquid N_2 then, a measure of the transition temperature can only be obtained through natural warming. An example of this type of curve appears in Figure 8. This curve shows an onset in superconductivity near 91K, with a significant volume fraction of the sample achieving superconductivity below 83K. The acquisition of helium will allow more numerous and extensive studies to be made.

Conclusion

Sb substitution into the Bi-system 2223 phase was successful, as determined to the limits of X-ray diffraction measurements. Transport measurements revealed no significant enhancement of the superconducting properties as previously reported for nominal compositions of this phase. Conclusive magnetic measurements will be conducted on these samples shortly.

A surprising melt-sintering effect was discovered in nominally substituted Sb/Bi/Pb compounds. Though these samples were initially multi-phased, melt-sintering conditions resulted in film-like regions on the surface of the samples. These "thick films" were c-axis oriented, and consisted of the Bi-system 2201, 2212, and 2223 phases. The actual presence of each phase could be controlled by the preparation conditions.

A vibrating sample magnetometer system was constructed and tuned. This system is capable of magnetic characterization of superconductors and will be used to investigate samples in this study as well as an archive of samples from previous work.

Figure 1

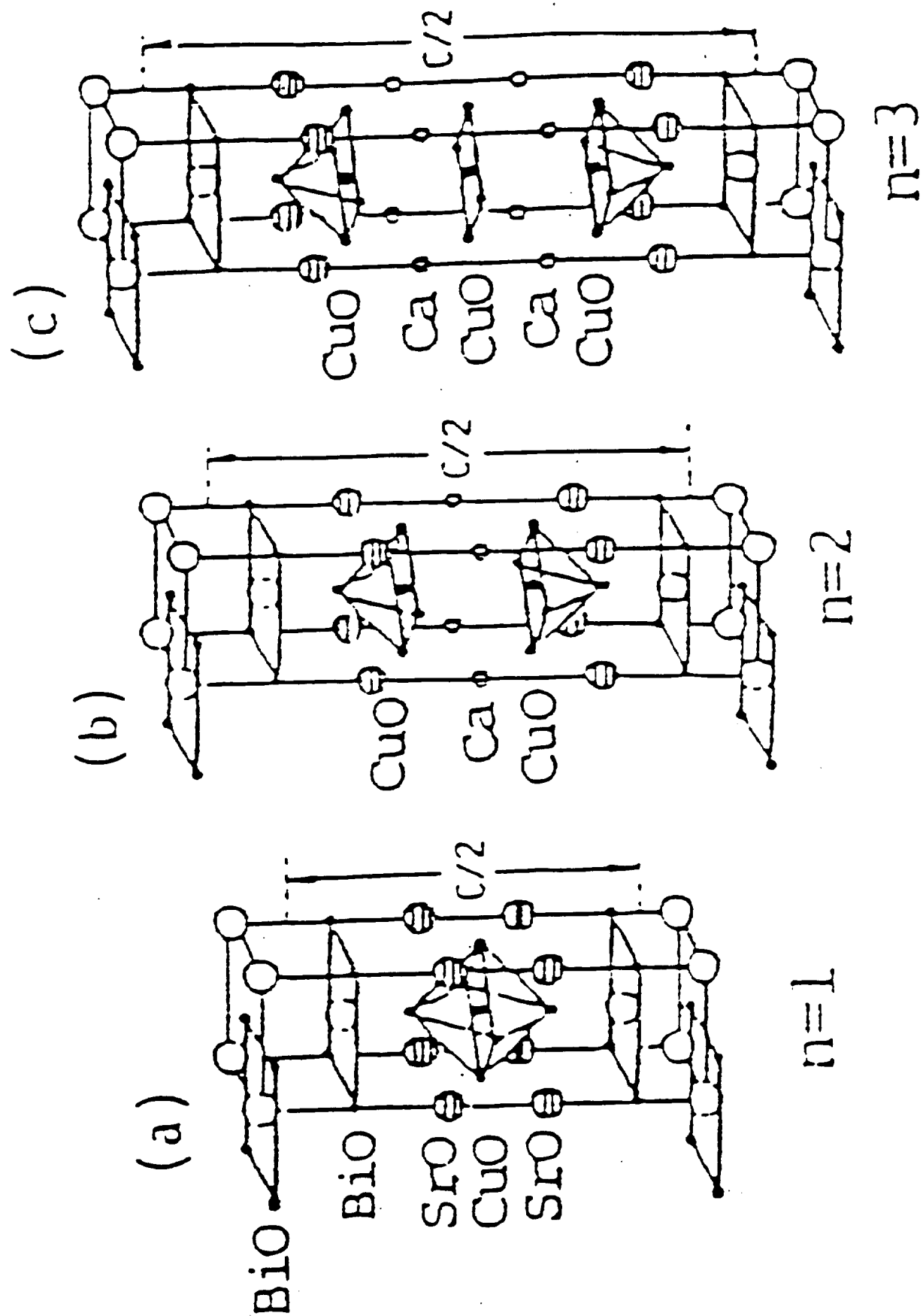
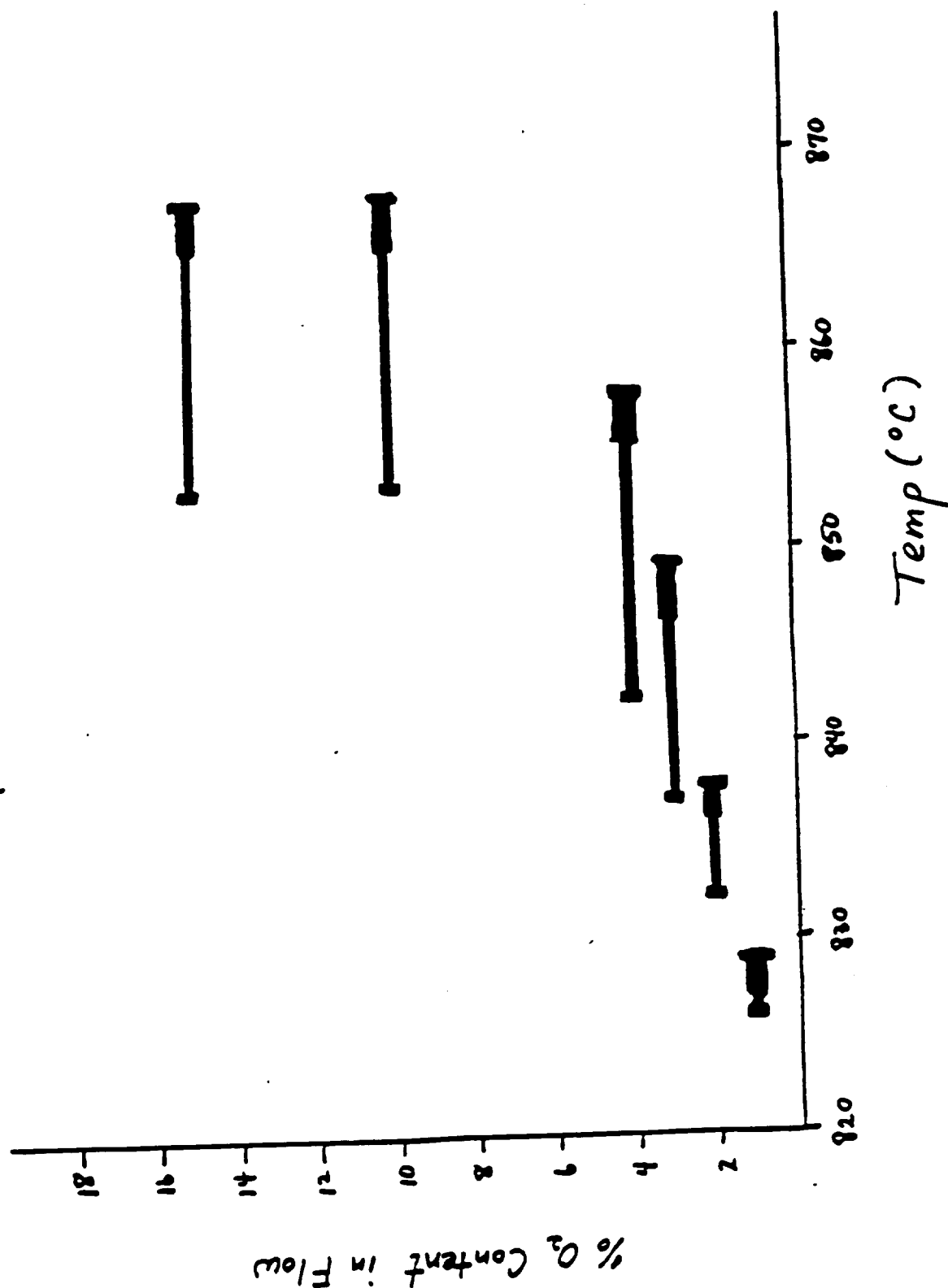


Figure 2

Formation of "2223" Phase as a Function of Temperature and O₂ content in Flow



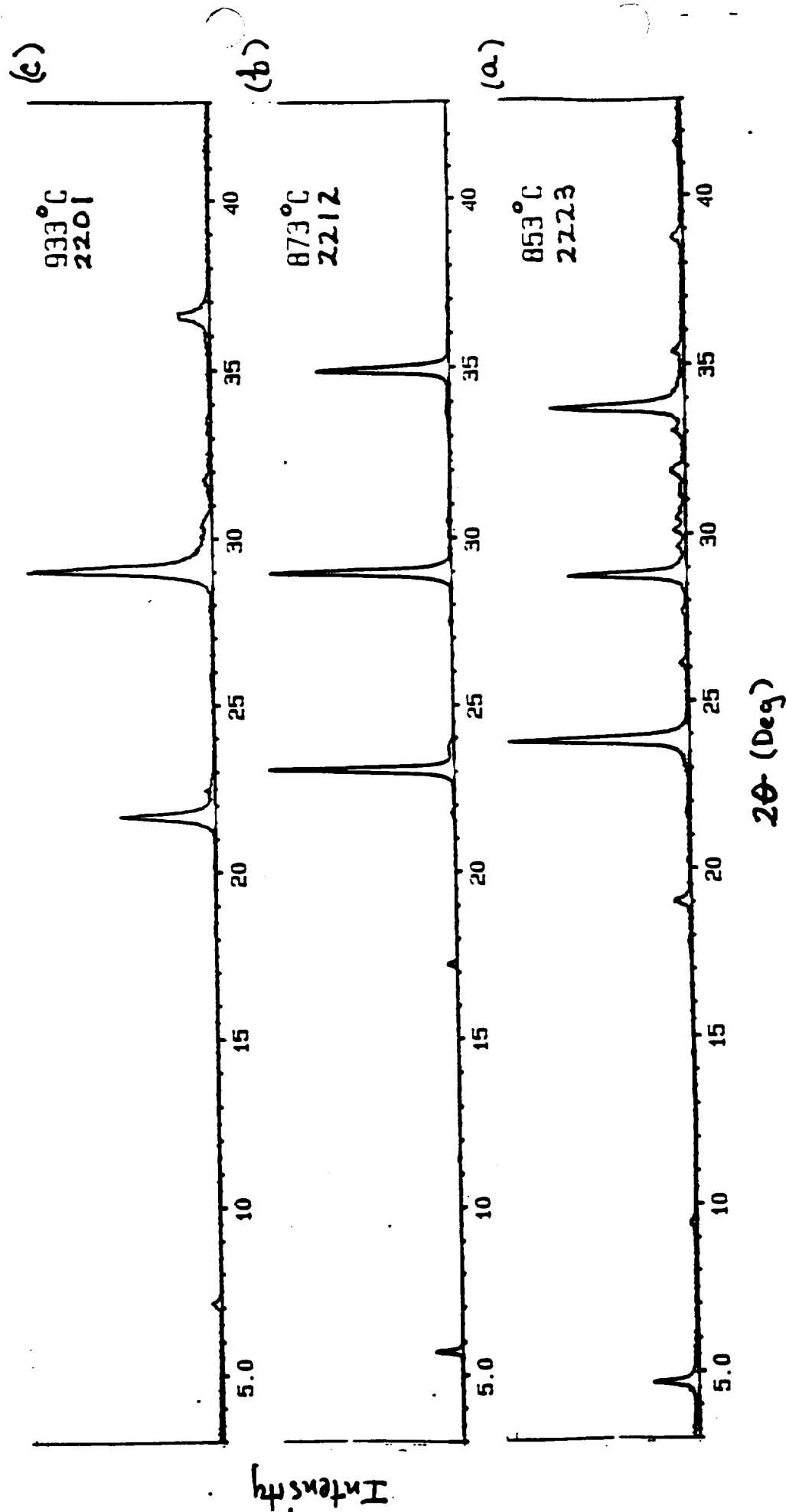
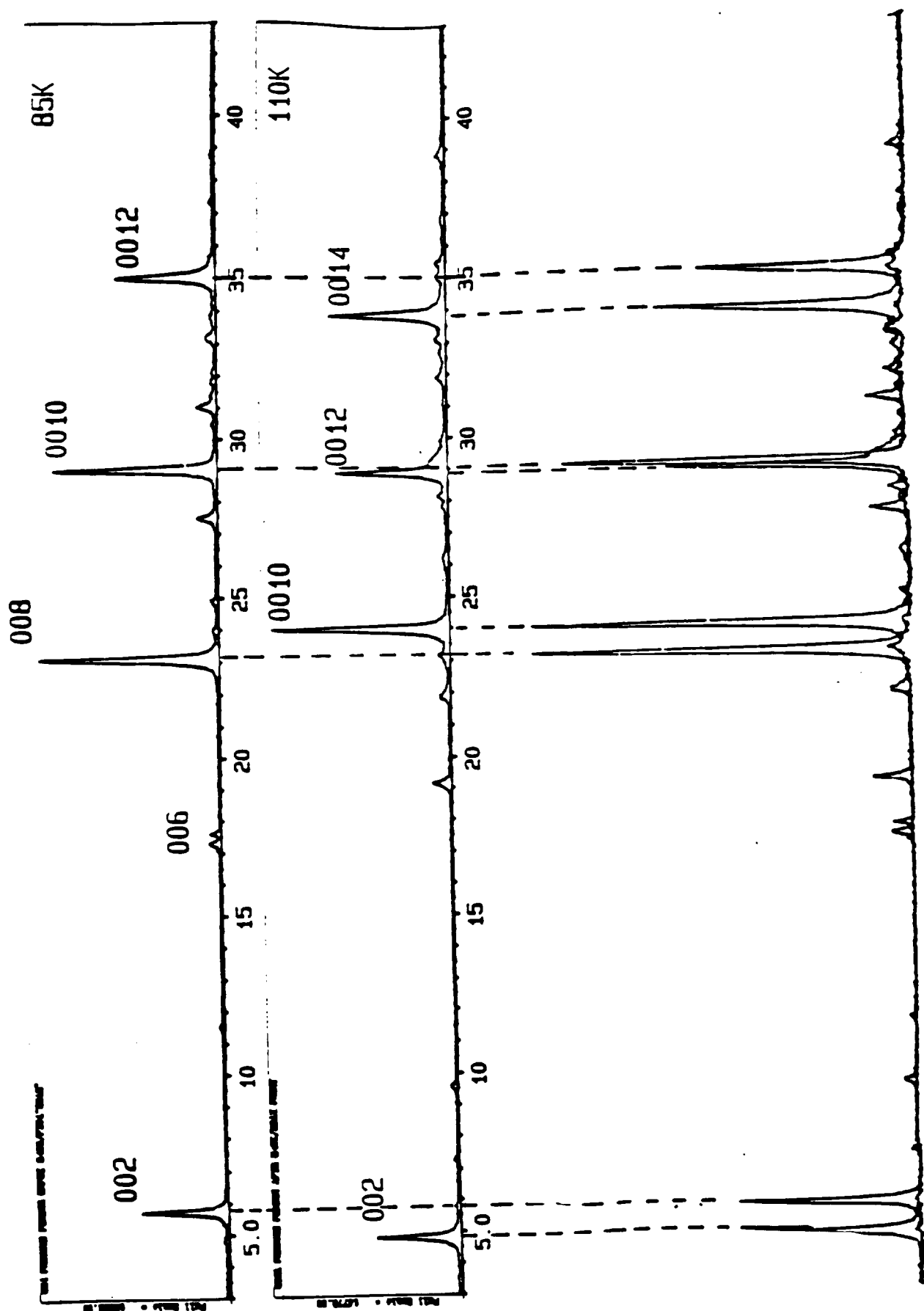


Figure 3

Figure 4



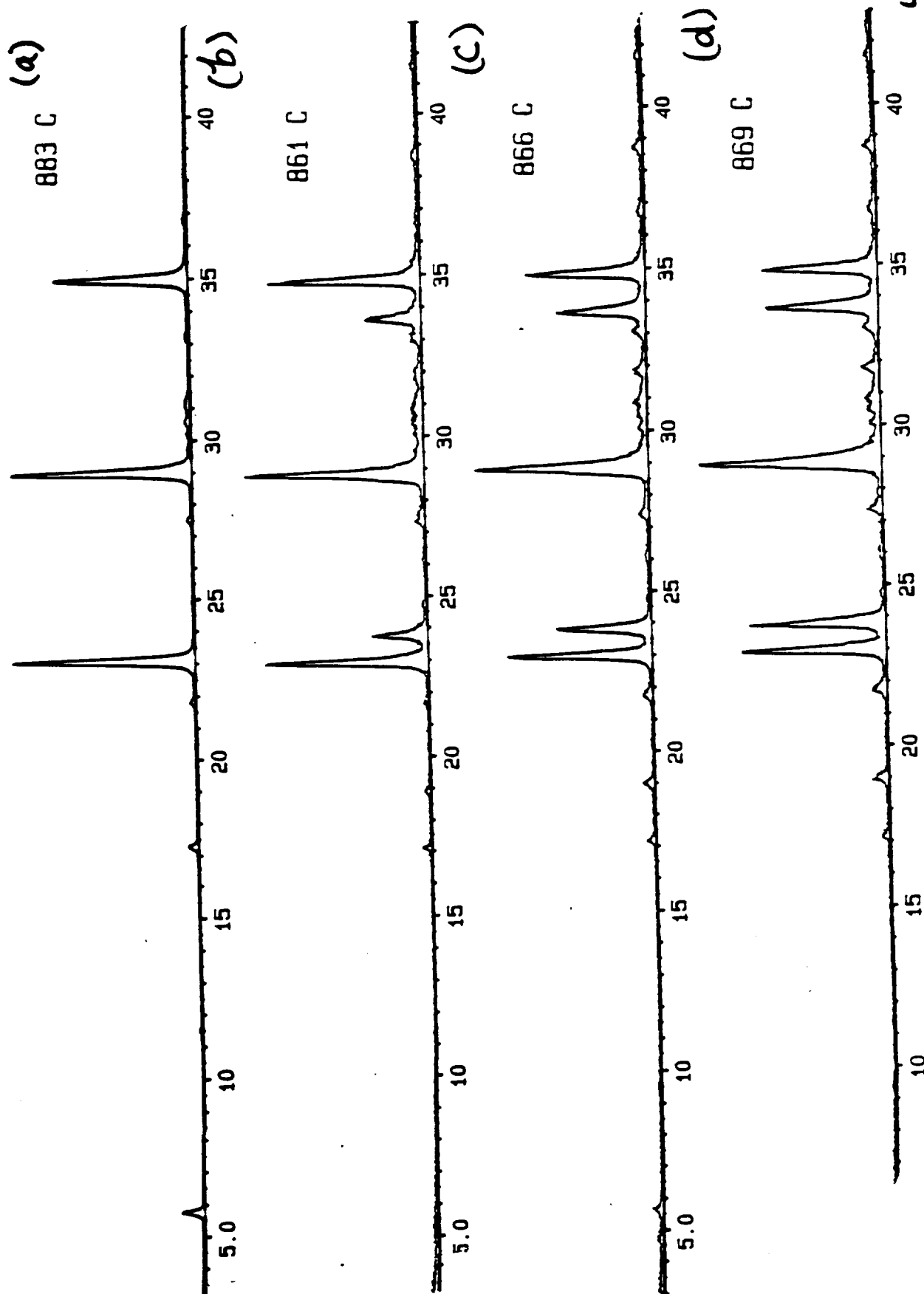


Figure 5

Figure 6

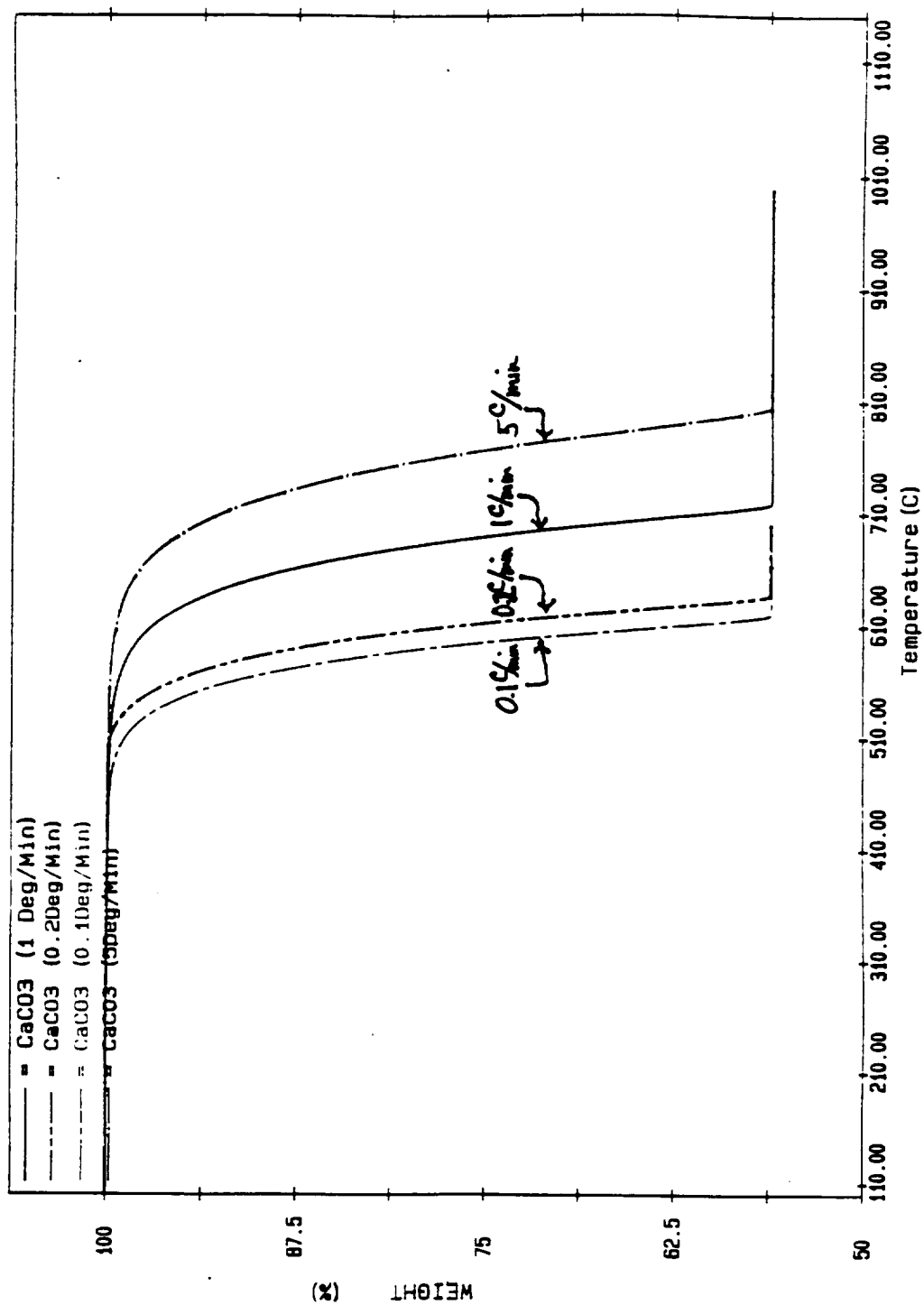


Figure 7

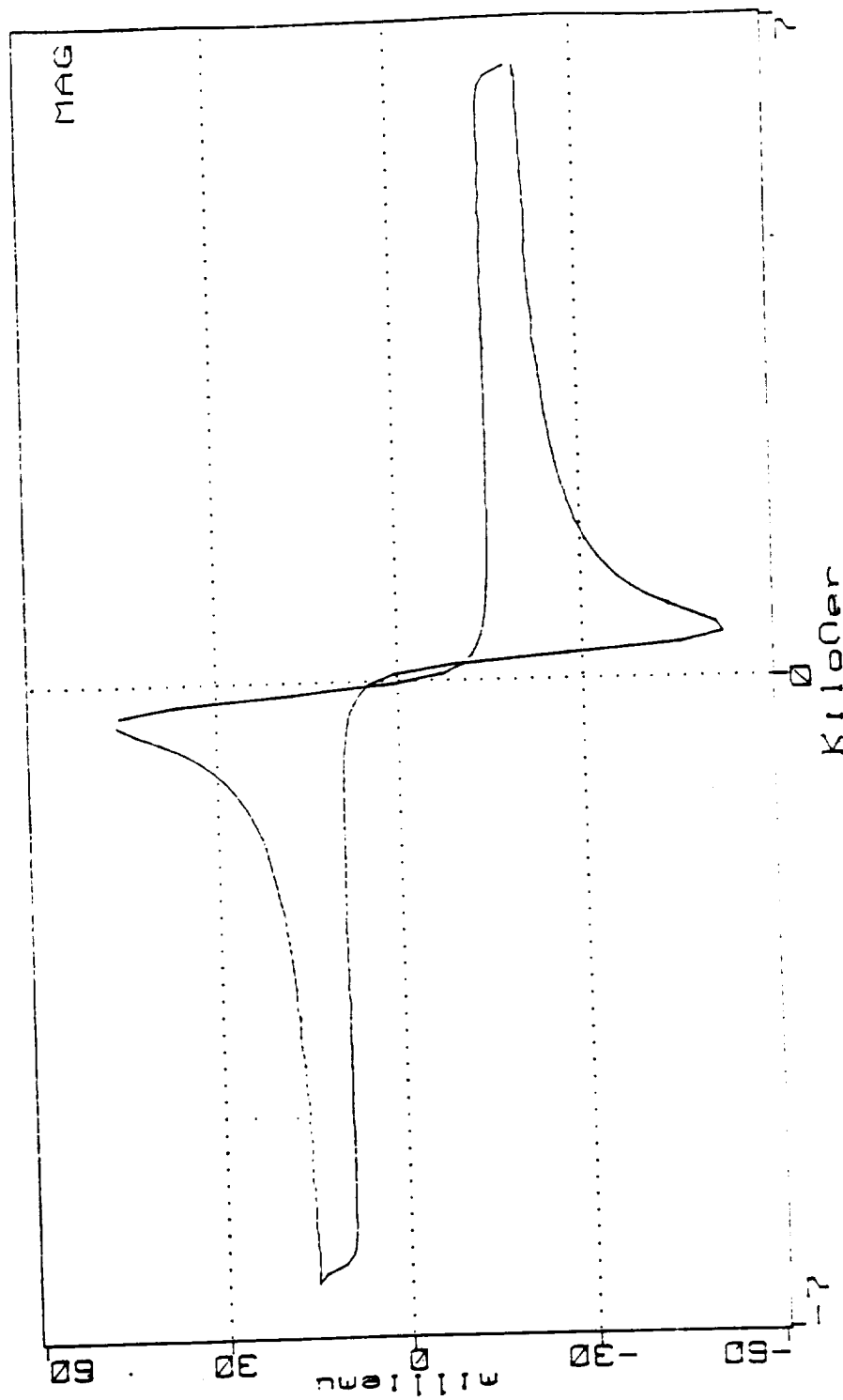
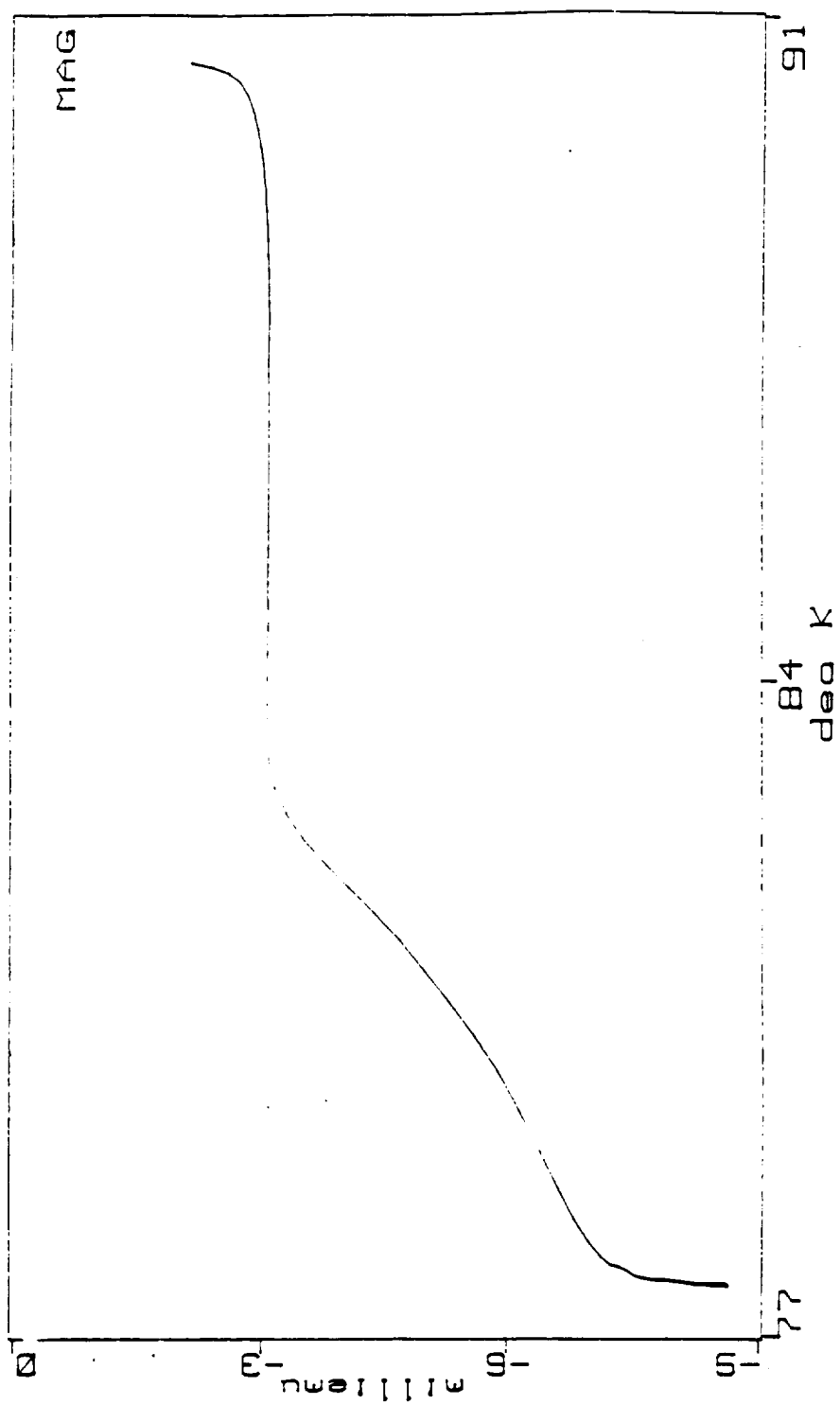


Figure 8



Superconducting Thin Film Deposition

After the discovery of high temperature superconducting (HTS) materials with transition temperatures as high as 125° K, many groups have been depositing and/or developing new techniques to deposit HTS thin films. Devices and sensors made from HTS are expected to have a major impact on superconducting electronics. This can only be accomplished by maximizing the quality of the films deposited such as the smoothness, critical current and transition temperature.

Most deposition techniques employed to deposit low temperature superconducting thin films have proven to be applicable to that of high temperature thin films. But the quality of the films varies as well as the techniques used. Sputtering, for example is an excellent technique for depositing Nb films and can also be used to deposit HTS $\text{YBa}_2\text{Cu}_3\text{O}_7$ thin films. The transition temperature of these films (60 - 80°K), however, is not as high as that of the bulk material ($\approx 95^\circ\text{K}$). The sputtered films also lack the smoothness desired because most require post annealing (600 to 850°C) to restore the superconducting property. Also, annealing causes film surface roughness. On the other hand, pulsed laser ablated films have demonstrated both smoothness and good transition temperature (83 - 94°K).

Laser ablation is a relatively new deposition technique which was never before applied to low temperature superconductor. The process is simple: a high energy pulse of U.V. laser light (1 to 2 J/ CM^2 , 12 nano seconds) vaporize the surface of the target material and coming off is a plume of gas material perpendicular to the target which coats a heated substrate. This technique was improved to accomodate the oxygen lost from $\text{YBa}_2\text{Cu}_3\text{O}_7$. A sustained oxygen discharge was added to the technique which is called plasma assisted laser ablation.

We have attempted to duplicate the technique for H & S thin films. Most of our effort has been spent in setting up the apparatus. The system was designed in-house and had to undergo many changes, as reported earlier, that would allow the laser light to be focused onto the surface of the target material. We did not produce any H & S thin films but did manage to deposit some material onto a glass

substrate while setting up the mirror. The coating also covered a mirror which later caused more changes. Designs were made so that the mirror could be mounted outside of the chamber. Results of this change are yet to be seen because the laser apparatus broke and awaits personnel from the company to repair it.

Finally, we expect the new changes to work. Films can possibly be produced within a month or two depending upon when the repair of the laser system occurs.

CONCLUSIONS

As covered in the report, new knowledge was gained in the quest to understand and produce new and better superconducting materials. Also, considerable progress was made in furthering the technology and capabilities needed to produce thin superconducting films by laser deposition techniques.

It is hoped that the work started on this and the previous Delivery Order may lead to better materials and processes sometime in the future. We regret the work's termination at this time but appreciate the opportunity afforded us to work on Delivery Orders 72 and 89.